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GLASS CERAMIC ENAMELS WITH INCREASED CONDUCTIVITY

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Based on crystallizing alkaline boron-titanium-silicate glasses with oxide additives of the R_2O type, ground and cover chemically stable enamels for steel have been developed, which exhibit high chemical resistance and high electrical conductivity.

Glass ceramic enamel coatings extensively used as protection from corrosion in kitchenware, household equipment, chemical equipment, and pipes are dielectric materials with ionic conduction determined by the presence of alkaline metal ions in these materials. The electrical insulating properties of enamel coatings depend on the coating quality, and the presence of defects in the coating continuity: pores, bubbles, microcracks, or extraneous conducting inclusions.

Among the industrial glass enamels, the best dielectric characteristics are exhibited by enamels for chemical equipment which, as a rule, are fused in two or more layers over steel articles and are subjected to 100% control for the existence of defects in continuity The volume electric resistance of such coatings exceeds $10^{12}\ \Omega \cdot$ cm. The good insulating properties of glass enamel coatings prevent electrostatic charge leak from the working surfaces of the equipment, which limits the use of enameled equipment in processing electrolyzed materials.

Nonmetallic equipment is regarded as electrostatically grounded, if the resistance of any point on its inner and outer surfaces with respect to the ground grid does not exceed $10^7\ \Omega$. Measurements of this resistance should be performed with a relative air humidity not more than 60%, whereas the surface area of the contact between the measuring electrode and the equipment surface should not exceed 20 cm^2 [1]. The volume resistance of enamel coating calculated taking into account the above conditions should not exceed $10^9\ \Omega \cdot$ cm.

The development of enamels with sufficient chemical stability and electrical resistance below $10^9\ \Omega \cdot$ cm was carried out based on glass ceramic materials in the $Na_2O - B_2O_3 - TiO_2 - SiO_2$ system. It was established [2] that within the specified system there is a certain glass-forming region in which rutile crystallizes under heat treatment. When such glasses are fired on a steel substrate, Ti^{4+} ions are partly reduced to Ti^{3+}, and the simultaneous crystallization of rutile results in a substantial decrease in the electric resistance of the entire coating [3].

The tetravalent titanium ions are intensely reduced inside the coating layers adjacent to the steel substrate and much less intensely in the other enamel layers, which produces an increase in the electrical resistance across the coating width. However, in coatings which are 100 – 200 μm thick these modifications are insignificant, and on the whole the electric resistance of undercoat enamel satisfies the set requirements.

The cover enamel was developed based on the specified glass system and modified with aluminum, potassium, zinc oxides to improve its chemical resistance. The purpose was to ensure the formation of rutile in sufficient quantity under additional heat treatment. To increase the conductivity of the crystalline phase (rutile) and of the coating on the whole, additives of one of the oxides (Nb_2O_5, Ta_2O_5, or Sb_2O_5) were introduced to the glass composition (0.2 – 0.5 mole %). These additives virtually do not alter the TCLE and electrical resistance of the initial glass T4-S, and to a certain extent improve its chemical resistance, especially on introduction of Sb_2O_5. Heat treatment of glasses at 850°C results in a substantial (4 – 5 orders of magnitude) decrease in the electrical resistance. It is established [4] that as the considered glasses are heated in the temperature interval of 750 – 925°C, rutile crystallizes in the melt, and Nb^{5+}, Sb^{5+}, or Ta^{5+} ions, which are similar to Ti^{4+} in their ionic radius size, are incorporated into the crystal lattice of rutile and form weakly bound conduction electrons in this lattice, which increases the electric conductivity of the crystalline phase and the glass ceramic material.

The electric resistance of the coating based on the considered glass with dopants Nb_2O_5 and Ta_2O_5 was significantly (3 – 4 orders of magnitude) lower than the resistance of the respective heat-treated glass. Thus, whereas the resistance of heat-treated glass T4-S containing 0.2% Nb_2O_5 at 20°C is equal to $10^9\ \Omega \cdot$ cm, the resistance of the respective two-coat enamel deposited on the primed steel surface is

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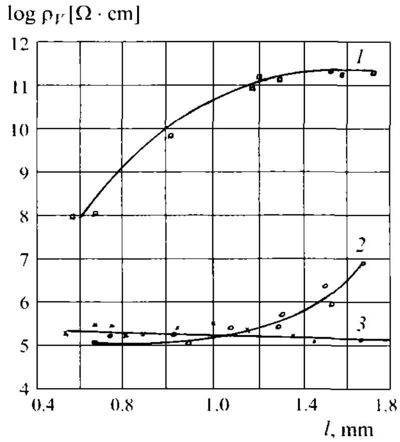

Fig. 1. Volume resistance ρ_V (at temperature 20°C) of the coating versus its width *l*: *1*, *2*, and *3*) coatings based on glass T4-S, glass T4-S + 0.2% Nb_2O_5 and glass T4-S + 0.2% Nb_2O_5 with introduction of 0.5 wt.% titanium to the slip, respectively.

10^5 Ω · cm. Apparently, the reducing processes taking place near the steel substrate has some effect under firing of the cover enamel as well, and along with the doping of rutile with Nb^{5+} ions, partial reduction of titanium dioxide takes place.

It is known [5] that a reducing medium facilitates the incorporation of type R^{5+} ions in the rutile lattice. As the coating thickness increases, the effect of the redox processes occurring in the boundary layer near the steel substrate decreases, which increases the volume resistance (Fig. 1, curve *2*). To create a weakly reducing medium in the course of enamel firing and thus stabilize the electric resistance across the width, a small quantity of a reducing agent, namely, metallic powder of aluminum, silicon, or titanium (0.3 – 0.5 wt.%) was added to the enamel slip. The specified additives had virtually no effect on the chemical resistance of the coating, but stabilized its electric conductivity under multiple firing (Fig. 1, curve *3*).

The low values of electric resistance and conduction activation energy and the presence and sign of thermoEDR are evidence of electronic conduction in the enamel coating

Properties of the developed cover enamel

Acid resistance (weight loss after 4 h of boiling in 20 and 24% HCl), mg/cm^2	0.17 – 0.31
Alkali resistance (weight loss after 4 h of boiling in 4% NaOH), mg/cm^2	1.1
Heat resistance, °C	280
Firing interval for coating, °C	820 – 900
Bulk electric resistance, Ω · cm	(2...5) × 10^5

Thus, the developed glass enamel coating is slightly inferior to the industrial enamel in its chemical resistance, but has significantly higher electric conductivity and can be used for enameling of chemical equipment and pipes, in which accumulation of static electricity on working surfaces is inadmissible.

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